On the Way to an Oxidative Hosomi–Sakurai Reaction

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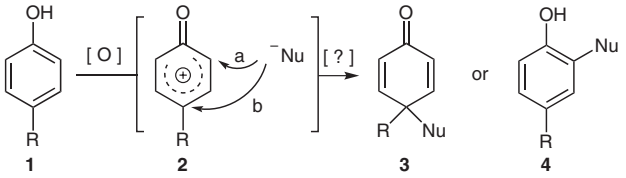
Abstract: An oxidative allylation process mediated by a hypervalent iodine reagent has been performed on polysubstituted phenols. This reaction, occurring in useful to good yields, leads to a rapid access to dienones containing a quaternary carbon center.

Key words: hypervalent iodine, allyltrimethylsilane, substitued phenols, oxidative allylation



Scheme 1

Allylation processes are generally recognized as important tools for organic synthesis; one of the most famous is the Hosomi–Sakurai reaction.[1] This reaction has opened up many new opportunities in synthetic chemistry. Indeed, the allyl moiety is known to be a good precursor of carbonyl. This reaction consists in the addition of mild nucleophiles such as allylsilanes, propargylsilanes, and enol ethers onto electrophilic species activated by Lewis acids. An interesting development of this reaction would be to extend its application to aromatic derivatives. A possible avenue to achieve this objective would involve the formation of an electrophilic intermediate from the corresponding aromatic ring. An indication of how this objective could be achieved is apparent in the work of Kita,[2] who has shown that phenols[3] may be activated under the influence of hypervalent iodine reagents such as iodobenzene diacetate[4] (DIB) leading to **2**. Electrophilic species **2** tends to react at the 4-position (cf. reaction mode b), at least with heteronucleophiles. We recently determined that carbon-based nucleophiles[5] in a bimolecular process attack the presumed intermediate **2** at a position adjacent to the carbonyl group (pathway a), resulting in the formation of product **4** (Scheme 1). As demonstrated by Kita,[6] this reaction generally occurs best in solvents such as trifluoroethanol (TFE) or hexafluoroisopropanol (HFIP). Formally, this type of transformation can be termed an 'aromatic ring umpolung'. While a phenol normally reacts as a nucleophile, suitable oxidative activation can convert it to reactive electrophilic intermediate **2**, which may be intercepted by mild nucleophiles.

Indeed on the basis of this concept, two reactions may be in competition: aromatic substitution (pathway a) versus oxidative addition (pathway b). Therefore, at this point, it would be interesting to verify the regioselectivity of mild nucleophiles such as allylsilanes with species such as **2**. One noteworthy similar approach has already been used in an intramolecular process as a key step in the synthesis of platensimycin[7] by Nicolaou et al. Moreover, a first approach to this reaction was developed by Quideau and coworkers[8] in aprotic solvents with phenyliodine bistrifluoracetate (PIFA), which has provided some noteworthy examples of oxidative allylation on substituted 1-naphthol. By generalizing and extending this reaction to different aromatic compounds in a bimolecular process, we would introduce novel opportunities in the field of chemical synthesis. Indeed, the corresponding dienone **3**, an interesting functionalizable core containing a prochiral quaternary center, can be easily dissymmetrized.[9] This main skeleton is present in numerous natural products: lycoramine,[10] platencin,[11] etc. To perform this reaction efficiently with phenols, different aspects must be considered. First, in protic and poorly nucleophilic solvents, such as TFE or HFIP (Kita's conditions), intermediate **2** should be stabilized by the solvent long enough to react with allylsilane. Second, the regioselectivity of the nucleophilic attack of allylsilane must be considered. As presented in Scheme 1, carbon-based nucleophiles, such as allylsilanes,[12] attack the presumed intermediate **2** at the least hindered position adjacent to the carbonyl group (pathway a). To perform an oxidative allylation process, it seems reasonable to block the *ortho* positions to avoid the cycloaddition process. Thus, to test the regioselectivity of the reaction, 2,4,6-trimethylphenol (**6**) was oxidized and led to a mixture (4:1) of **7** and **8** in 41% yield (Scheme 2).

Although a mixture of compounds **7** and **8** was obtained, this result is encouraging because it demonstrates the feasibility of this approach. In order to increase the selectivity, it seems rational to use adequate bulky groups, such as *tert*-butyl, to conduct the reaction exclusively at one position. Under these conditions, the desired dienones are produced in high yield (Scheme 3). Indeed, such hindered structures have already been used efficiently in oxidative dearomatization of phenols.[13] These structures appear to be good precursors for an efficient oxidative Hosomi–Sakurai-type process. Additionally, this reaction seems to occur as well in the *ortho* or *para* positions. These exper-

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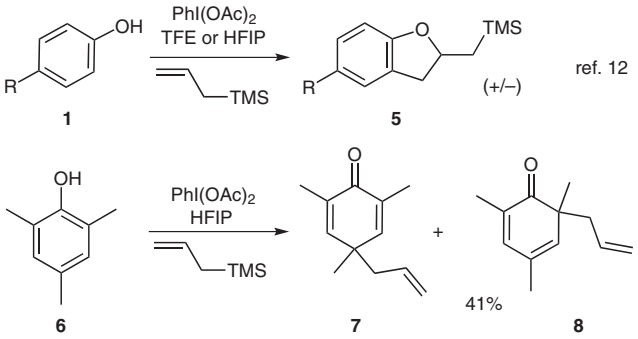


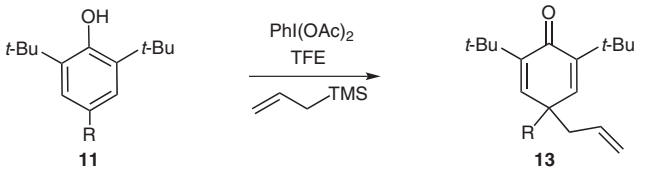
Scheme 2

iments have demonstrated that the steric effect of the substituents controls the regioselectivity of this reaction. The reaction seems more efficient when the attack occurs in the *para* position.

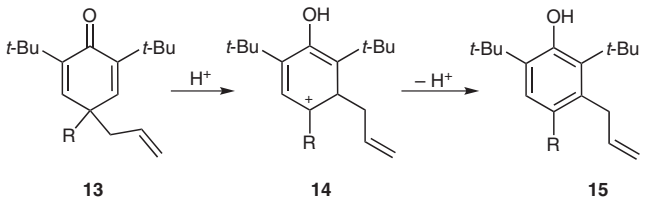
Since compound **11** is more substituted than compound **1**, its oxidation occurs more slowly due to the presence of bulky substituents in the *ortho* positions; in some cases it is difficult to convert all the starting materials. However, this reaction provides higher yields of the desired products. This observation could be rationalized considering that potential electrophilic intermediate **12** would be more stable than the species **2** due to the presence of two additional electron-donor groups. As expected, the ratio of byproducts has decreased significantly. To extend the scope of this reaction, different 4-alkyl-2-6-di-*tert*-butyl phenols **11** were successfully oxidized. A summary of representative experiments appears in Table 1.[14] It is worthy of note that the reaction tolerates moderately nucleophilic functionalities such as alcohols, sulfonamides, and esters.

The source of hypervalent iodine, iodobenzene diacetate, is a key aspect of this reaction. Indeed, during the process, it releases 2 equivalents of acetic acid, promoting some dienone–phenol rearrangement.[15] While this rearrangement occurs slowly with acetic acid, it can be accelerated in the presence of stronger acids such as trifluoroacetic acid. This may be the reason why PIFA would not be the most appropriate oxidizing reagent (Scheme 4).

Table 1 Representative Experiments for the Oxidation of 4-Alkyl-2-6-di-*tert*-butyl Phenols **11**

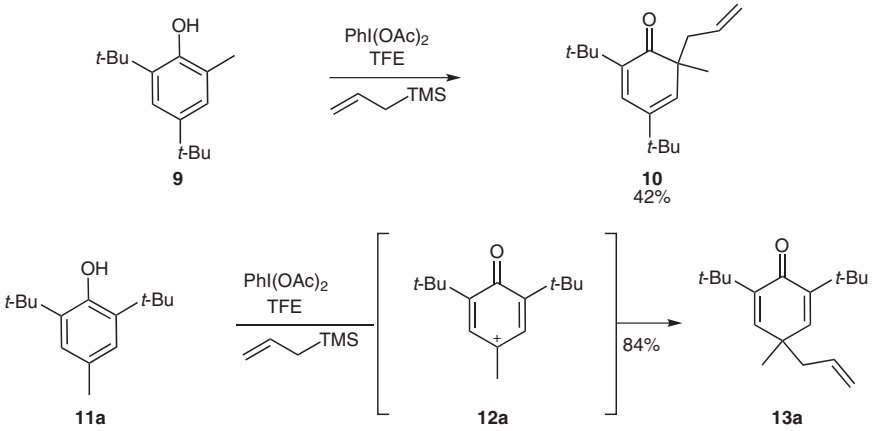


Entry	**11**	R	Yield of **13** (%)
1	**11a**	Me	**13a** 84
2	**11b**	*n*-Pent	**13b** 79
3	**11c**	*i*-Pr	**13c** 74
4	**11d**	CH_2CH_2OH	**13d** 71
5	**11e**	$CH_2OTBDMS$	**13e** 81
6	**11f**	CH_2CH_2NHTs	**13f** 61
7	**11g**	CH_2CO_2Me	**13g** 70



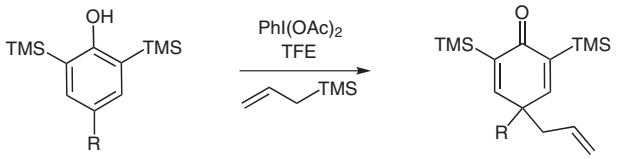
Scheme 4

In order to avoid being restricted to *tert*-butyl groups, we have investigated possible protective groups that would have the potentiality to block the desired positions while being subsequently removable. An interesting choice would be the halides: as a matter of fact, they could be efficiently introduced onto an aromatic ring. In particular, bromides could be useful to generate some C–C bonds by means of palladium chemistry. This synthetic strategy could be useful for the total synthesis of numerous natural products. Unfortunately, oxidation of 2-6-dibromo cresol led to inextricable byproducts. However, bromides can



Scheme 3

Table 2 Treatment of Di-TMS-phenols under Oxidative Conditions

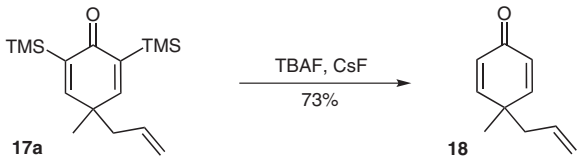


16 17

Entry	16	R	Yield of 17 (%)
1	**16a**	Me	**17a** 52
2	**16b**	Et	**17b** 46
3	**16c**	Ph	**17c** 37
4	**16d**	CH_2CH_2OH	**17d** 41

easily be changed into a trimethylsilyl group,[16] a motif quite similar to *tert*-butyl with the advantage of being easily removable. Consequently, different di-TMS-phenols have been treated under the oxidative conditions. A summary of representative experiments appears in Table 2.[17]

While this reaction also proceeds with trimethylsilyl groups, it remains less efficient than with their *tert*-butyl analogues. Compounds that have partially lost one or two trimethylsilyl groups were recovered as byproduct. However, oxidation of **16** appears synthetically useful to generate functionalizable structures such as **18**. Indeed, **17a** easily produces **18** in 73% yield under a TBAF/CsF treatment (Scheme 5).



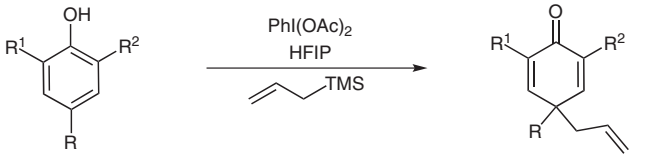
17a 18

Scheme 5

The trimethylsilyl group appears to be a suitable protective group for this reaction and contributes to the development of a general oxidative allylation process for phenols. To explore the scope and limit of this reaction, we were interested in combining different protective groups. Hence various mixed phenols were oxidized. While the oxidation of di-halogen-phenols is not efficient, a combination of halogen and *tert*-butyl or trimethylsilyl groups produces the desired compound **21** in useful yield (Table 3). It should be noted that compound **20e**,**f** can be easily obtained from the dibrominated phenols[16] and the subsequent oxidation quickly leads to highly polyfunctionalized cores **21e**,**f**.[18] They may be useful for rapid access to the total synthesis of numerous natural products. They appear to be the best compromise for potential further applications.

Regarding compound **20**, no addition has been observed on the carbon containing the halide. The selectivity observed might be explained by the fact that the mesomer

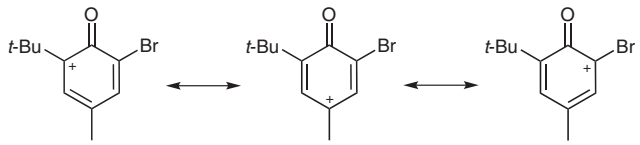
Table 3 Synthesis of Compound **21**



20 21

Entry	20	R	R^1	R^2	Yield of 21 (%)
1	**20a**	Me	Cl	*t*-Bu	**21a** 65
2	**20b**	Me	Br	*t*-Bu	**21b** 51
3	**20c**	Me	I	*t*-Bu	**21c** 45
4	**20d**	*i*-Pr	Br	*t*-Bu	**21d** 42
5	**20e**	Me	Br	TMS	**21e** 53
6	**20f**	*n*-Bu	Br	TMS	**21f** 52

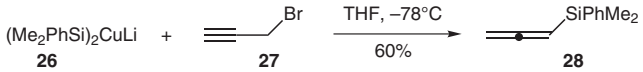
form **25** is a weaker contributor to the overall delocalized system (Scheme 6). Indeed, alkyls are known to be better electron-donor groups than halides. The use of TFE as solvent in reactions involving **20** results in the formation of an important part of the addition of TFE on the substrate (compound **3**, pathway b, Scheme 1, in agreement with Kita's observations).[6] This problem can be easily avoided by using a less nucleophilic solvent such as HFIP.



23 24 25

Scheme 6

Moreover, this process can be extended to alennyltrimethylsilane **28**. The latter was easily afforded for the first time by treatment of the Fleming silylcuprate reagent[19] with propargyl bromide in 60% yield (Scheme 7).



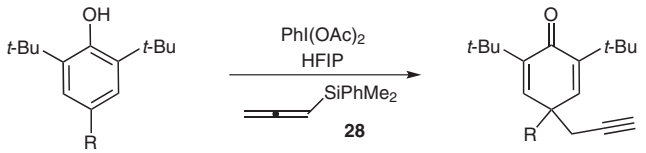
26 27 28

Scheme 7

A summary of representative oxidative experiments with **28** and different polysubstitued phenols appears in Table 4.[20] However, this process is inefficient with halogenoalkene such as 2-bromoallyltrimethylsilane. This result could be explained due to the withdrawing effect of the halogen, which deactivates the nucleophilic character of the alkene moiety.

In conclusion, an approach to accomplish an oxidative allylation process extended to phenols is now available. The transformation provides new strategic opportunities in the chemical synthesis of substances, and results in ongoing

Table 4 Summary of Representative Oxidative Experiments with Compound **28**



11 **29**

Entry	**11**	R	Yield of **29** (%)
1	**11a**	Me	**29a** 81
2	**11h**	*n*-Bu	**29h** 77
3	**11i**	$CH_2CH_2CHCH_2$	**29i** 75

investigations; their applications in total synthesis of natural products will be disclosed in due course.

Experimental Procedure

To a stirred solution of phenol (0.2 mmol) in TFE or HFIP (0.5 mL) at r.t. was added allylsilane (137 mg, 1.2 mmol, 6 equiv), followed DIB (97 mg, 0.3 mmol, 1.5 equiv) dissolved in TFE or HFIP (0.4 mL) over 20 s (Table 3). After 10 min stirring, 64–97 mg of DIB (from 1–1.5 equiv) in TFE or HFIP (0.25 mL) were added to the reaction mixture, depending of the phenol side chain. The solution was stirred for further 5 min and quenched with sat. aq $NaHCO_3$ (2 mL). The aqueous phase was extracted with EtOAc (3×5 mL), washed with brine (5 mL), dried over Na_2SO_4 and concentrated. The crude product was purified by chromatography (*n*-hexane–CH_2Cl_2).

Acknowledgment

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(14) **Analytical Data**

IR: ca. 1645 (CO) cm^{-1}.

Compound **13b**: ^1H NMR (300 MHz, $CDCl_3$): δ = 6.33 (s, 2 H), 5.43 (m, 1 H), 4.92 (m, 2 H), 2.23 (d, 2 H, *J* = 7.8 Hz), 1.53 (m, 2 H), 1.19 (m, 22 H), 0.99 (m, 2 H), 0.80 (t, 3 H, *J* = 6.6 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 187.3, 148.2, 145.7, 133.5, 118.1, 45.3, 44.1, 40.1, 35.1, 32.4, 29.9, 24.3, 22.7, 14.2. ESI-HRMS: *m/z* calcd for $C_{22}H_{36}ONa$ $[M + Na]^+$: 339.2658; found: 339.2662.

Compound **13c**: ^1H NMR (300 MHz, $CDCl_3$): δ = 6.39 (s, 2 H), 5.43 (m, 1 H), 4.93 (m, 2 H), 2.32 (d, 2 H, *J* = 7.5 Hz), 1.83 (h, 1 H, *J* = 6.6 Hz), 1.21 (s, 18 H), 0.84 (d, 6 H, *J* = 6.6 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 187.4, 148.8, 144.3, 133.8, 117.8, 46.4, 42.4, 36.3, 35.3, 29.9, 18.2. ESI-HRMS:

m/z calcd for $C_{20}H_{33}O$ [M + H]$^+$: 289.2525; found: 289.2529.
Compound **13d**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.44 (s, 2 H), 5.48 (m, 1 H), 4.97 (m, 2 H), 3.42 (t, 2 H, *J* = 7.2 Hz), 2.30 (d, 2 H, *J* = 7.8 Hz), 1.92 (t, 2 H, *J* = 7.2 Hz), 1.27 (s, 18 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 186.9, 148.4, 145.0, 132.7, 118.8, 60.0, 45.4, 42.9, 42.8, 35.2, 29.8 ESI-HRMS: *m/z* calcd for $C_{19}H_{30}O_2Na$ [M + Na]$^+$: 313.2138; found: 313.2138.
Compound **13e**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.50 (s, 2 H), 5.49 (m, 1 H), 4.97 (m, 2 H), 3.48 (s, 2 H), 2.35 (d, 2 H, *J* = 7.2 Hz), 1.22 (s, 18 H), 0.88 (s, 9 H), 0.03 (s, 6 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 187.2, 148.8, 143.0, 133.4, 118.3, 69.1, 45.7, 40.5, 35.2, 29.9, 26.1, 18.5, –5,1. ESI-HRMS: *m/z* calcd for $C_{24}H_{43}O_2Si$ [M + H]$^+$: 391.3026; found: 391.3008.
Compound **13f**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56 (d, 2 H, *J* = 7.5 Hz), 7.20 (d, 2 H, *J* = 7.5 Hz), 6.25 (s, 2 H), 5.35 (m, 1 H), 4.87 (m, 2 H), 4.29 (m, 1 H), 2.55 (q, 2 H, *J* = 6.6 Hz), 2.32 (s, 3 H), 2.17 (d, 2 H, *J* = 7.5 Hz), 1.79 (t, 2 H, *J* = 6.6 Hz), 1.10 (s, 18 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 186.5, 149.1, 144.2, 144.0, 136.6, 132.3, 130.1, 127.3, 119.0, 45.3, 43.1, 40.1, 39.7, 35.2, 29.8, 21.8. ESI-HRMS: *m/z* calcd for $C_{26}H_{37}NO_3SNa$ [M + Na]$^+$: 466.2386; found: 466.2378.
Compound **13g**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.49 (s, 2 H), 5.50 (m, 1 H), 4.01 (m, 2 H), 3.54 (s, 3 H), 2.54 (s, 2 H), 2.35 (d, 2 H, *J* = 7.2 Hz), 1.21 (s, 18 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 186.7, 170.7, 148.1, 143.4, 132.5, 119.3, 51.7, 44.6, 44.3, 42.0, 35.2, 29.8. ESI-HRMS: *m/z* calcd for $C_{20}H_{31}O_3$ [M + H]$^+$: 319.2267; found: 319.2267.

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(17) **Analytical Data**
Compound **17a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.86 (s, 2 H), 5.52 (m, 1 H), 4.99 (m, 2 H), 2.26 (d, 2 H, *J* = 7.2 Hz), 1.20 (s, 3 H), 0.16 (s, 18 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 192.0, 162.4, 140.7, 133.3, 118.6, 45.2, 41.4, 25.5, –0.9. ESI-HRMS: *m/z* calcd for $C_{16}H_{29}OSi_2$ [M + H]$^+$: 293.1751; found: 293.1753.
Compound **17b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.77 (s, 2 H), 5.51 (m, 1 H), 4.99 (dd, 1 H, *J* = 8.7, 1.2 Hz), 4.96 (dd, 1 H, *J* = 18.0, 1.2 Hz), 2.29 (d, 2 H, *J* = 7.2 Hz), 1.63 (q, 2 H, *J* = 7.8 Hz), 0.68 (t, 3 H, *J* = 7.8 Hz), 0.16 (s, 18 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 192.4, 161.3, 143.0, 133.3, 118.3, 46.1, 44.3, 32.1, 9.3, –0.8. ESI-HRMS: *m/z* calcd for $C_{17}H_{31}OSi_2$ [M + H]$^+$: 307.1908; found: 307.1909.
Compound **17c**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30 (m, 5 H), 7.00 (s, 2 H), 5.56 (m, 1 H), 5.05 (m, 2 H), 2.80 (d, 2 H, *J* = 7.2 Hz), 0.18 (18 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 192.1, 160.7, 141.1, 140.8, 132.9, 129.3, 127.6, 127.0, 119.0, 48.6, 42.3, –0.9. ESI-HRMS: *m/z* calcd for $C_{21}H_{31}OSi_2$ [M + H]$^+$: 355.1908; found: 355.1914.
Compound **17d**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.86 (s, 2 H), 5.47 (m, 1 H), 4.98 (m, 2 H), 3.42 (t, 2 H, *J* = 6.9 Hz), 2.29 (d, 2 H, *J* = 7.2 Hz), 1.92 (t, 2 H, *J* = 6.9 Hz), 0.14 (s, 18 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 192.1, 160.9, 142.7, 132.5, 119.1, 60.0, 44.7, 44.4, 42.0, –0.9. ESI-HRMS: *m/z* calcd for $C_{17}H_{31}O_2Si_2$ [M + H]$^+$: 323.1857; found: 323.1853.

(18) **Analytical Data**
Compound **21a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.91 (d, 1 H, *J* = 2.7 Hz), 6.55 (1 H, d, *J* = 2.7 Hz), 5.55 (m, 1 H), 5.04 (m, 2 H), 2.34 (d, 2 H, *J* = 8.1 Hz), 1.27 (s, 3 H), 1.23 (s, 9 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 179.1, 149.1, 149.0, 145.4, 133.8, 132.5, 119.5, 45.3, 42.9, 35.3, 29.5, 25.6. ESI-HRMS: *m/z* calcd for $C_{14}H_{20}ClO$ [M + H]$^+$: 239.1197; found: 239.1185.
Compound **21b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.18 (d, 1 H, *J* = 3.0 Hz), 6.56 (d, 1 H, *J* = 3.0 Hz), 5.53 (m, 1 H), 5.04 (m, 2 H), 2.33 (d, 2 H, *J* = 6.9 Hz), 1.27 (s, 3 H), 1.22 (s, 9 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 178.9, 153.6, 149.0, 145.1, 132.5, 126.4, 119.5, 45.1, 44.4, 35.4, 29.5, 25.5. ESI-HRMS: *m/z* calcd for $C_{14}H_{20}BrO$ [M + H]$^+$: 283.0692; found: 283.0688.
Compound **21c**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50 (d, 1 H, *J* = 2.7 Hz), 6.57 (d, 1 H, *J* = 2.7 Hz), 5.54 (m, 1 H), 5.04 (m, 2 H), 2.32 (d, 1 H, *J* = 6.9 Hz), 2.29 (d, 1 H, *J* = 7.8 Hz), 1.27 (s, 3 H), 1.21 (s, 9 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 179.6, 161.9, 149.3, 143.8, 132.5, 119.5, 107.6, 46.1, 45.0, 35.5, 29.5, 25.3. ESI-HRMS: *m/z* calcd for $C_{14}H_{20}IO$ [M + H]$^+$: 331.0553; found: 331.0549.
Compound **21d**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.16 (d, 1 H, *J* = 2.7 Hz), 6.55 (1 H, d, *J* = 2.7 Hz), 5.47 (m, 1 H), 5.01 (m, 2 H), 2.40 (m, 2 H), 1.93 (hept, 1 H, *J* = 6.6 Hz), 0.93 (d, 3 H, *J* = 6.6 Hz), 0.89 (d, 3 H, *J* = 6.6 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 179.3, 151.8, 147.4, 147.1, 132.6, 127.6, 119.1, 51.4, 41.8; 36.2, 35.7, 29.6, 18.4, 18.2. ESI-HRMS: *m/z* calcd for $C_{16}H_{23}BrO_2Na$ [M + Na]$^+$: 333.0824; found: 333.0822.
Compound **21e**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.21 (d, 1 H, *J* = 3.0 Hz), 6.89 (d, 1 H, *J* = 3.0 Hz), 5.55 (m, 1 H), 5.05 (m, 2 H), 2.33 (d, 2 H, *J* = 7.2 Hz), 1.27 (s, 3 H), 0.18 (s, 9 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 181.7, 162.9, 154.9, 139.6, 132.3, 125.4, 119.6, 46.0, 44.7, 25.0, –1.1. ESI-HRMS: *m/z* calcd for $C_{13}H_{19}BrOSiNa$ [M + Na]$^+$: 321.0280; found: 321.0278.
Compound **21f**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.16 (d, 1 H, *J* = 2.7 Hz), 6.84 (d, 1 H, *J* = 2.7 Hz), 5.53 (m, 1 H), 5.03 (m, 2 H), 2.35 (d, 2 H, *J* = 7.2 Hz), 1.65 (t, 2 H, *J* = 9.0 Hz), 1.25 (m, 2 H), 1.10 (m, 2 H), 0.85 (t, 3 H, *J* = 7.2 Hz), 0.19 (s, 9 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 182.1, 162.4, 154.3, 141.3, 132.2, 126.1, 119.4, 50.4, 44.1, 38.9, 27.2, 23.3, 14.1, –1.1. ESI-HRMS: *m/z* calcd for $C_{16}H_{25}BrOSiNa$ [M + Na]$^+$: 363.0750; found: 363.0752.

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(20) **Analytical Data**
Compound **29a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.52 (s, 2 H), 2.33 (d, 2 H, *J* = 2.3 Hz), 2.03 (t, 1 H, *J* = 2.3 Hz), 1.28 (s, 3 H), 1.23 (s, 9 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 186.1, 146.6, 144.7, 79.8, 71.2, 38.5, 34.6, 30.9, 29.4, 25.3. ESI-HRMS: *m/z* calcd for $C_{18}H_{27}O$ [M + H]$^+$: 259.2056; found: 259.2042.
Compound **29h**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.44 (s, 2 H), 2.34 (d, 2 H, *J* = 2.3 Hz), 2.00 (t, 1 H, *J* = 2.3 Hz), 1,68 (t, 2 H, *J* = 8.2 Hz), 1.23 (s + q, 20 H, *J* = 8.2 Hz), 1.00 (sext, 2 H, *J* = 8.2 Hz), 0.84 (t, 3 H, *J* = 8.2 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 186.5, 148.1, 143.8, 79.7, 71.1, 42.3, 38.3, 34.8, 30.2, 29.4, 26.5, 22.9, 13.8. ESI-HRMS: *m/z* calcd for $C_{21}H_{33}O$ [M + H]$^+$: 301.2526; found: 301.2533.
Compound **29i**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.44 (s, 2 H), 5,73 (m, 1 H), 4.96 (d, 1 H, *J* = 18.7 Hz), 4,93 (d, 1 H, *J* = 10.5 Hz), 2.37 (d, 2 H, *J* =2.3 Hz), 2.03 (t, 1 H, *J* = 2.3 Hz), 1.81 (t, 2 H, *J* = 8.2 Hz), 1.43 (t, 2 H, *J* = 8.2 Hz), 1.24 (s, 18 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 186.4, 148.5, 143.3, 127.6, 114.8, 79.5, 71.4, 42.2, 37.7, 34.9, 30.4, 29.4, 28.8. ESI-HRMS: *m/z* calcd for $C_{21}H_{31}O$ [M + H]$^+$: 299.2369; found: 299.2376.